Communication to the Editor

A novel route for the preparation of narrow particle size distribution emulsions and microcapsules†

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Abstract: A process is described for making emulsions, and microcapsules derived from them, of known, narrow particle size distribution. This can greatly reduce problems of thermodynamic instability and degradation, and improve biological performance by permitting close control of the release rate of capsules.

Keywords: emulsions; microcapsules; narrow size distribution

1 INTRODUCTION

Oil-in-water emulsions (EW) are important as pesticide formulations that are more environmentally friendly than are emulsifiable concentrates (EC). With water as the continuous phase, there is usually no flash point, and the products are often less dermally toxic than their EC counterparts. Once prepared, EW can be combined with suspension concentrates (SC) into suspo-emulsions (SE). It is well established that emulsions are thermodynamically unstable and tend to degrade over time, and the same is true for SEs. However, these problems can be greatly reduced if the particle size and particle size distribution can be controlled during processing. A narrow size distribution may also be important in targeting the dissolved active ingredients biologically, and it will also improve long-term stability by reducing Ostwald ripening.

In addition to being a useful formulation type in themselves, oil-in-water emulsions are the precursors to microencapsulated materials. When making capsules, the size distribution of the emulsion determines (within the error of most measurement methods) the size distribution of the resulting capsules. This is because the capsule wall thickness is usually small and the density of the capsule wall polymer not too greatly different from that of the starting materials. The release rate of capsules is profoundly influenced by their particle size, and a distribution of size leads to a distribution of release rates. Monodispersity of the starting emulsion leads to a similarly monodisperse disperse distribution for the capsules. This is desirable because of the control over release rate that can thus be achieved. We here report a means of making emulsions and capsules with very narrow particle size distributions. The method that we employ has a further, possibly more important, benefit. It allows us to calculate and thus manipulate beforehand the exact size of the finished emulsion, and thus to achieve any capsule or emulsion size required, with great precision.

The basis of the method is to use a polymeric latex particle as a 'template' for the emulsion. The oil of which it is desired to make an emulsion is added to the chosen latex suspension, usually with the addition of surfactant. The surfactant aids in stabilising the latex during the addition of the oil, and also assists in transporting the added oil to the latex particles. Not only does the use of latex templates provide a means of making essentially monodisperse capsules (by virtue of the ready availability of monodisperse latex suspensions), but also confers on the emulsion so formed a greatly enhanced stability, which is desirable in itself, and makes formulating SE (suspo-emulsions) notably easier.

2 MATERIALS AND METHODS

Most of the work reported here was done using poly(styrene) latex particles as model systems, with chlorpyrifos dissolved in xylene as the oil phase. However, a wide variety of active ingredients and oils can be formulated in the same way. The surfactant of choice was Atlox 4991 (ICI Surfactants), an alcohol

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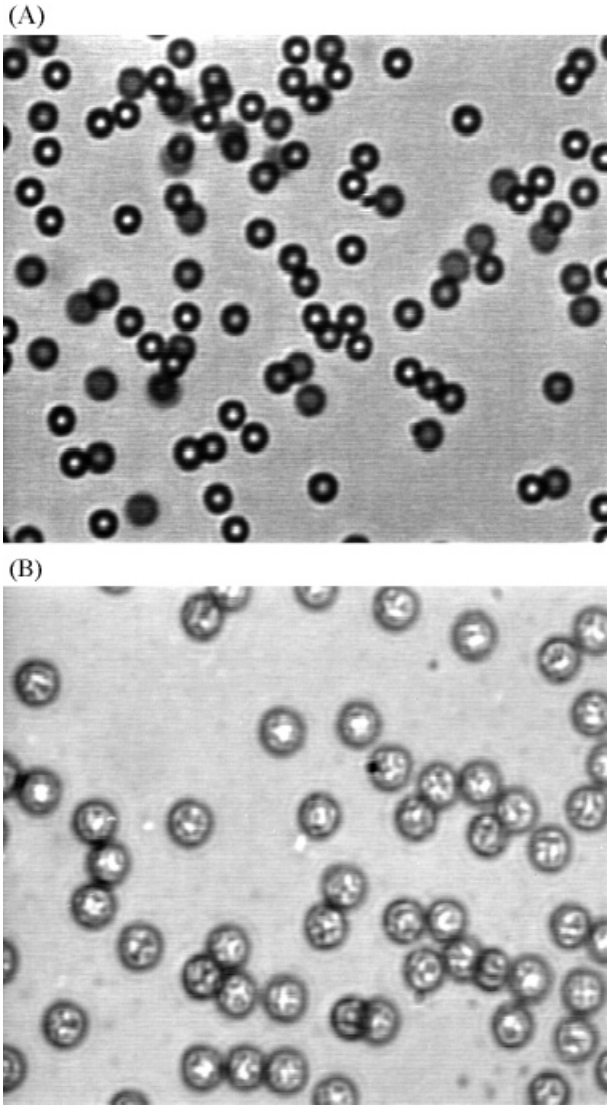

Figure 1. (A) Initial latex and (B) final capsule suspension.

ethoxylate, but many other non-ionic surfactants were found to work very well. The addition of a small amount of anionic surfactant such as sodium diisooctylsulphosuccinate was found to increase the rate of equilibration in some cases.

The polymer latex was used without dilution – more concentrated latex suspensions equilibrated more rapidly, and thus were more convenient experimentally. The same final state was attained using low concentrations, but the rate of equilibration was very much slower. Also, the state of sub-division of the added oil was important in governing the rate of equilibration, with larger interfacial areas (smaller drop sizes) giving higher rates.

The particle size and particle size distributions were determined using either Malvern Mastersizer or Malvern Zetasizer instruments, using the software supplied with these instruments to reduce the data. In the case of the Mastersizer, the presentation code used for the polystyrene latex material was generally 1000, but the resulting capsule suspension was measured using 0807. It was advantageous to use the monomodal setting, although this was not essential.

3 RESULTS

3.1 Addition of oil to the latex

Narrow particle size distribution poly(styrene) latices were used in this work as model systems. The span of the poly(styrene) latex shown in Figure 1 is 0.26, and the VMD (volume median diameter) is 2.25 μm using 1000 as the presentation code. This result was confirmed by electron microscopy, and also by using the Coulter Counter. The large size of the template latex allowed the use of optical microscopy to confirm the measurements obtained with the Mastersizer. This latex then had approximately 700% of oil (xylene + chlorpyrifos) added (based on the volume of latex) to bring the particle size to 4.77 μm. The original latex is shown in Fig 1A The monodispersity is visually apparent.

3.2 Calculation of final size

When the oil is added to the latex, the size (judged by the VMD) is accurately predictable. The basis of this predictability is that the total volume V_{TOTAL} (oil + latex) is combined into a uniform sphere, and

		Mean diameter (nm)		
Latex[a]	*Added oil*[b]	*Calculated*	*Measured*	*Polydispersity/span*
S/B	CPF/xyl	276	286	0.144
S/B	CPF/xyl	191	192	0.051
S/B	CPF/xyl	289	293	0.042
S	Solvesso 200	1670	1640	0.2 (span)
S	CPF/xyl + PAPI	3870	3700	0.75 (span)
S	CPF/xyl + Dowanol	2250	2250	Oil removed—same as base latex
S	CPF/xyl	237	238	0.06
S	CPF/xyl	283	292	0.077
S	CPF/xyl	455	455	0.165

Table 1. Characteristics of latex-based emulsions

[a] S/B = Styrene/butadiene.
[b] Xyl = xylene; CPF = chlorpyrifos.

R, the radius of that sphere is:

$$V_{\mathrm{TOTAL}} = V_{\mathrm{OIL}} + V_{\mathrm{LATEX}}$$

where

$$V_{\mathrm{TOTAL}} = 4\pi R^3/3,$$

and thus R can be calculated. Results for a number of latices and oils given in in Table 1.

In one case, after the oil (chlorpyrifos dissolved in xylene) had been added, and the size verified to be as predicted, 20% Dowanol DPM was added, and immediately (within 1 min) the oil was removed from the latex, and the VMD was that previously obtained for the starting latex. This ease of removal, together with the speed of deposition of the oil, suggests that coating rather than imbibition is the prime initial mechanism for this process. With the passage of time, the oil is expected to imbibe fully.

3.3 Encapsulation of the emulsion

Next, instead of adding just the oil phase, an appropriate amount of isocyanate (PAPI 135; Aldrich) was dissolved in the oil phase before this was added to the latex. When the equilibration was complete (5 min) a water-soluble amine (diethylene triamine, DETA) was added to react interfacially with the isocyanate. Capsules were produced by the interfacial polycondensation reaction. These capsules had essentially the same VMD and span as the latex + oil phase, and there was no detectable shrinkage or expansion as the interfacial reaction went to completion. The resultant capsule suspension is shown in Fig 1B.

These capsules were compared biologically with a commercial chlorpyrifos 480 g liter^{-1} EC (Dursban 4EC). Capsules are expected to slow the release of the encapsulated material, and hence to reduce the 'knockdown' effect. Unexpectedly, the initial biological activity of the encapsulated material was superior to that of the EC. The differences became more accentuated as time elapsed, and at both seven and 14 days after treatment (DAT), the performance of the capsules was clearly superior. This superiority was emphasized in a semi-field trial, where, up to 12 DAT, the capsules significantly outperformed the EC.

4 DISCUSSION AND CONCLUSIONS

Latices have been employed to produce extremely stable oil-in-water emulsions (EW). The mechanism of this stabilisation is thought to be the coating of the oil onto the latex particle which subsequently becomes swollen as the added oil is fully imbibed. The resultant stable latex-based emulsions have also been transformed into suspo-emulsions which have improved physical stability when compared to a conventional SE.

Probably more significant is the ability to take these physically stable, calculable-sized emulsions, and transform them into capsules. These capsules have been demonstrated to have the same size as the precursor emulsion within the error of the detection method, and thus can also be of calculable and accurately controllable size, as well as being essentially monodisperse.

The resulting microencapsulated products, having a very narrow particle size distribution, have consistent release characteristics through the polymeric wall (since all the particles are of the same size, and thus all the capsule walls are of the same thickness). This offers the potential of precise control of the release rates of such microencapsulated products, which is expected to be of use both in agriculture and other technologies.